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ATTORNEY'S DOCKET NUMBER
514413-3852

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (If known see 37 C.F.R. 1.5)

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

(EARLIEST) PRIORITY DATE CLAIMED

PCT/EP99/04581

July 2, 1999

July 10, 1998

TITLE OF INVENTION

**PROCESS FOR THE PREPARATION OF 2-AMINO-4-CHLORO-1,3,5-
TRIAZINE**

APPLICANT(S) FOR DO/EO/US

**Jürgen ZINDEL, Jens HOLLANDER, Klemens MINN and Lothar
WILLIMS**

Applicants herewith submit to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
- ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
- ☐ This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).
- ☒ The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
- ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
- ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
- ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
- ☐ A English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
- ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
- ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 16 below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
- ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☐ Other items or information:

PCT/IB/306, 308, one page Abstract

PCT/ISA/210

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Chun-wei Tseng
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Chun-wei Tseng
(Signature of person mailing paper or fee)

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.59)

INTERNATIONAL APPLICATION NO.

PCT/EP99/04581

ATTORNEY'S DOCKET NO.

514453-3852

17. ☒ The following fees are submitted

(CALCULATIONS - PTO USE ONLY)

Basic National Fee (37 CFR 1.492(a)(1)-(5)):

Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO. **\$1,000.00**

International preliminary examination fee (37 C.F.R. 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO. **\$ 860.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but
international search fee (37 CFR 1.445(a)(2)) paid to USPTO. **\$ 710.00**

International preliminary examination fee paid to USPTO (37 CFR 1.482)
but all claims did not satisfy provisions of PCT Article 33(1)-(4) **\$ 690.00**

International preliminary examination fee paid to USPTO (37 CFR 1.482)
and all claims satisfied provisions of PCT Article 33(1)-(4) **\$ 100.00**

ENTER APPROPRIATE BASIC FEE AMOUNT = (\$ 860.00)

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

<u>10</u> Claims	/Number Filed	/	Number Extra	/Rate	(\$
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Total Claims	/ <u>10</u> - 20 =	/	<u>0</u>	/X \$18.00	(\$
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Independent Claims	/ <u>1</u> - 3 =	/	<u>1</u>	/X \$80.00	(\$ 0.00
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MULTIPLE DEPENDENT CLAIM(S) (if applicable)	/+ \$270.00	(\$
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TOTAL OF ABOVE CALCULATIONS = (\$ 860.00)

☒ Applicant claims small entity status. See 37 C.F.R. 1.27. The fees indicated above
are reduced by 1/2.

(\$

SUBTOTAL = (\$860.00)

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).

+

TOTAL NATIONAL FEE = (\$ 860.00)

Fee for recording the enclosed assignments (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **\$40.00** per property + (\$

TOTAL FEES ENCLOSED = (\$ 860.00)(Amount to be:
refunded.

\$

(charged:

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a. ☒ A check in the amount of **\$860.00** to cover the above fees is enclosed.b. ☐ Please charge my Deposit Account No. _____ in the amount of \$_____ to cover the above fees.c. ☒ A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit
Account No. **50-0320**. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the
application to pending status.

SEND ALL CORRESPONDENCE TO:

SIGNATURE

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William F. Lawrence
NAME

28,029

REGISTRATION NUMBER

Dated: December 12, 2000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s) : ZINDEL et al.
U.S. Serial No. : Filed Concurrently Herewith
Int'l Appln. No. : PCT/EP99/04581
Int'l Filing Date : 2 July 1999
Earliest Priority Date : 10 July 1998
For : PROCESS FOR THE PREPARATION OF 2-AMINO-4-
CHLORO-1,3,5-TRIAZINES

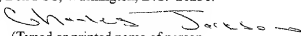
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New York, NY 10151

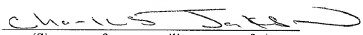
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Date of Deposit: December 12, 2000

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PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Box PCT
Washington, D.C. 20231

Dear Sir:

Preliminary to the examination of this U.S. national phase application, please enter the following amendments:

IN THE CLAIMS:

Claim 3, line 1, please delete "or 2";

Claim 4, line 1, please delete "any of claims 1 to 3" and insert --claim 1--;

Claim 5, line 1, please delete "any of claims 1 to 4" and insert --claim 1--;

Claim 6, line 1, please delete "any of claims 1 to 5" and insert --claim 1--;

Claim 7, line 1, please delete "any of claims 1 to 6" and insert --claim 1--;

Claim 8, line 1, please delete "any of claims 1 to 7" and insert --claim 1--;

Claim 5, line 1, please delete "any of claims 1 to 4" and insert --claim 1--;

Claim 9, line 14, please delete "any of claims 1 to 3" and insert --claim 1--;

Please cancel claim 11 without prejudice.

REMARKS

This application includes multiple claim dependencies. The amendment removes the multiple claim dependencies, and the filing fee for this application was computed on the basis that no dependent claim depends from more than one preceding claim. Claim 11 was deleted during the international preliminary examination.

Entry of this amendment and an early examination on the merits are respectfully solicited.

Respectfully submitted,

FROMMER LAWRENCE & HAUG LLP

By:



William F. Lawrence
Reg. No. 28,029
(212) 588-0800

Description

Processes for the preparation of 2-amino-4-chloro-1,3,5-triazines

The invention relates to the technical field of the chemical synthesis of bioactive compounds, preferably the processes for the preparation of crop protection agents and intermediates for these processes.

It has been disclosed that 2-amino-4-chloro-1,3,5-triazines which are substituted by organic radicals in the 6-position on the triazine ring can be employed for preparing bioactive aminotriazines, for example herbicidal aminotriazines, the chlorine atom being exchanged for an N-substituted amino radical; cf. WO-A-90/09378, WO-A-96/25404, WO-A-97/00254, WO-A-97/08156, WO-A-97/19936, WO-A-97/29095, WO-A-97/31904, WO-A-97/35481, WO-A-98/10654, WO-A-98/15536, WO-A-98/15537, WO-A-98/15538, WO-A-98/15539; moreover, aminotriazines have been proposed in International Application No. PCT/EP98/00283 and in German Patent Application No. 19826670.7.

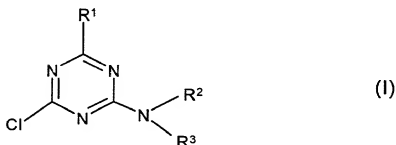
The substituted 2-amino-4-chloro-1,3,5-triazines can be obtained in accordance with a known process from the suitably substituted 2,4-dichloro-1,3,5-triazines and ammonia, or amines [J. Med. Chem. 12 (1969) 41, J. Am. Chem. Soc. 82 (1960) 3760]. The 6-substituted 2,4-dichloro-1,3,5-triazines, which are employed as starting compounds for this purpose, can be prepared, for example, from cyanuric chloride and Grignard compounds which are substituted in the 6-position on the triazine ring like the organic radical [Helv. Chim. Acta 33 (1950) 1368]. Alternatively, they can be synthesized from trichloromethyl isocyanide dichloride and amidines which are substituted in the 6-position on the triazine ring like the organic radical (cf. DE-A-1178437).

The disadvantages of the known processes are the limited availability, in particular the lack of availability of the Grignard compounds for the

preparation of triazines with alkyl radicals in the 6-position, and frequently poor yields when reacting the dichlorotriazines with ammonia or amines.

It is an object of the invention to prepare in an alternative and preferably advantageous manner 2-amino-4-chloro-1,3,5-triazines which have unsubstituted or substituted aliphatic hydrocarbon radicals in the 6-position. This is also intended to make available some novel triazines of the formula (I).

The invention relates to a process for the preparation of compounds of the formula (I) or salts thereof



in which

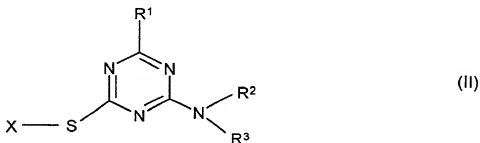
R^1 is (C_1-C_8) alkyl or (C_3-C_8) cycloalkyl, where each of the two above radicals independently of the other is unsubstituted or substituted, preferably unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, hydroxyl, cyano, nitro, thiocyanato, formyl, (C_1-C_8) alkoxy, (C_1-C_8) alkylthio, (C_1-C_8) alkylsulfinyl, (C_1-C_8) alkylsulfonyl, $[(C_1-C_8)\text{-alkyl}]$ carbonyl, $[(C_1-C_8)\text{alkoxy}]$ carbonyl, (C_2-C_8) alkenyl, (C_2-C_8) alkynyl, (C_3-C_8) cycloalkyl, phenyl and, in the case of cycloalkyl, also (C_1-C_8) alkyl, each of the last-mentioned 11 radicals being unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, (C_1-C_4) alkoxy, (C_1-C_4) alkylthio and, in the case of cyclic radicals, also (C_1-C_4) alkyl and (C_1-C_4) haloalkyl, and

R^2 , R^3 in each case independently of one another are hydrogen, amino,

hydroxyl, formyl or unsubstituted or substituted (C₁-C₈)alkyl, (C₁-C₈)alkylamino, di[(C₁-C₈)alkyl]amino, (C₁-C₈)alkyloxy, aryl, aryloxy, (C₃-C₈)cycloalkyl, [(C₁-C₈)alkyl]carbonyl, [(C₁-C₈)alkoxy]-carbonyl, arylcarbonyl, aryloxy carbonyl, (C₁-C₈)alkylsulfonyl, arylsulfonyl or an unsubstituted or substituted heterocyclyl radical, heterocyclyloxy radical, heterocyclylamino radical, each of which has 3 to 6 ring atoms and 1 to 3 hetero ring atoms selected from the group consisting of N, O and S, or

R², R³ together with the nitrogen atom of the group NR²R³ are a heterocyclic radical having 3 to 6 ring atoms and 1 to 4 hetero ring atoms, where, in addition to the nitrogen atom, the other hetero ring atoms which may exist are selected from the group consisting of N, O and S and the heterocycle is unsubstituted or substituted,

which comprises converting 2-amino-4-thio-1,3,5-triazines of the general formula (II)



in which X represents hydrogen, (C₁-C₆)alkyl, (C₂-C₆)alkenyl, (C₂-C₆)alkynyl or phenyl, where each of the last-mentioned 4 radicals is unsubstituted or substituted, or represents a 2-amino-4-thio-1,3,5-triazine radical which is bonded via sulfur and equally substituted by chlorination into the compound (I).

The 2-amino-4-thio-1,3,5-triazines (II), which act as starting materials, are known or can be prepared analogously to known processes [cf. DE-A-4139624, Chem. Ber. 100 (1967) 1874-1891, J. Heterocyclic Chem. 27 (1990) 1565-1568, J. Heterocyclic Chem. 23 (1986) 1709-1714].

A chlorinating agent is required in the process according to the invention, for example chlorine, salts of hypochlorous acid, phosphorus pentachloride,

phosphoryl chloride (=phosphorus oxychloride) or thionyl chloride, preferably chlorine.

The chlorinating agent is employed, for example, in amounts of 1 to 100 equivalents based on the compound of the formula (II), preferably 1 to 10 equivalents, in particular in equimolar amounts up to an excess, which allows a reaction of the compound of the formula (II) to take place. An equivalent in this context is to be understood as meaning such an amount of chlorinating agent which is required for reacting the compound (II) according to stoichiometrical reasons.

In principle, the chlorination reaction can be carried out without additional solvent and/or diluent (hereinbelow both: solvent), or, most expediently, in the presence of a solvent. Suitable solvents are preferably organic solvents which are largely inert to the chlorinating agent and the compounds of the formulae (II) and (I) under the reaction conditions. Examples of suitable solvents are:

1. Predominantly aprotic organic solvents which are inert under the reaction conditions, for example

- aliphatic and aromatic hydrocarbons such as, for example, mineral oils, petroleum ether, cyclohexane or toluene, xylenes, naphthalene derivatives, ®Solvesso 200 (high-boiling aromatic mixture);
- halogenated aliphatic and aromatic hydrocarbons such as methylene chloride, dichloroethane, chloroform or chlorobenzene;
- cyclic or open-chain ethers such as diethyl ether, di-n-propyl ether, diisopropyl ether, methyl tert-butyl ether, tetrahydrofuran (THF), dioxane, alkylene glycol monoalkyl ethers and alkylene glycol dialkyl ethers such as, for example, propylene glycol monomethyl ether, propylene glycol monoethyl ether, ethylene glycol monomethyl ether or ethylene glycol monoethyl ether, dimethoxyethane, diglyme, triglyme and tetraglyme;
- amides such as dimethylformamide (DMF), dimethylacetamide and N-methylpyrrolidone;
- ketones such as cyclohexanone, methyl isobutyl ketone (MIBK);

- nitriles such as acetonitrile, propionitrile, butyronitrile and benzonitrile;
 - sulfoxides and sulfones such as dimethyl sulfoxide (DMSO) and sulfolane,
 - carboxylic esters such as the esters of mono-, di- and tricarboxylic acids with aliphatic alcohols having 1 to 10 carbon atoms, for example ethyl formate, methyl acetate, ethyl acetate, n-propyl acetate, i-propyl acetate, esters of acetic acid with n-, i-, sec- or tert-butanol;
 - mixtures of two or more of the abovementioned solvents;
2. Essentially anhydrous, preferably largely anhydrous, protic solvents and their mixtures or mixtures with the abovementioned aprotic solvents. Examples of protic solvents are
- aliphatic alcohols such as methanol, ethanol, n- or i-propanol, n-, i-, sec- or tert-butanol, glycols;
 - carboxylic acids, for example those having 1 to 4 carbon atoms such as formic acid, acetic acid, n-propionic acid or n- and isobutanoic acid.

If the compounds of the formula (II) are chlorinated with chlorine, especially suitable solvents are, for example, methylene chloride, chloroform and concentrated acetic acid, preferably the corresponding anhydrous solvents such as, for example, glacial acetic acid.

The reaction can be carried out within a wide temperature range, in some cases depending on the substrate, the chlorinating agent and the solvent, for example at temperatures between -40°C and the boiling point of the solvent in question, preferably between -20°C and 100°C, in particular between 0°C and 50°C. The reaction temperature should be low enough to avoid side reactions, but high enough to allow a conversion within technically feasible reaction times.

As regards the pressure, particular conditions are not required; as a rule, it

is possible or expedient to carry out the chlorination reaction under atmospheric pressure.

Generally customary methods may be employed for working up the reaction mixture. After the reaction, it is possible, for example, to pass an inert gas, for example nitrogen gas, through the mixture so as to remove excess chlorine gas, and subsequently to pour the reaction mixture into water. The product is separated from the water and dried.

If the chlorination reaction is carried out in the presence of solvents which are miscible with water, such as, for example, carboxylic acids, the reaction mixture is preferably put into an aqueous solution of a base. If the chlorination reaction is carried out in the presence of solvents which are not miscible with water such as, for example, halogenated hydrocarbons, a base which is not soluble in this solvent is preferably added to the reaction mixture after chlorination, and the mixture is filtered and the product separated from the solvent and dried. Suitable bases are customary organic and, preferably, inorganic bases, and aqueous solutions of these, for example hydroxides or carbonates of alkali metals or alkaline earth metals.

Some chlorination reactions of 2-amino-4-alkylthio-1,3,5-triazines are already known, but the triazines are substituted by aromatic radicals in the 6-position on the triazine ring. Thus, chlorination reactions for the preparation of 2,4-dichloro-6-(2-pyridyl)-1,3,5-triazine [Tetrahedron 31 (1975) 1879-1882] or of 2-chloro-4,6-bis(2',4'-dimethylphenyl)-1,3,5-triazine [US-A-5084570] from the corresponding alkylthio-1,3,5-triazines have already been described. The conditions for the chlorination reaction which are given in the known protocols cannot be simply used for the 2-amino-4-thio-1,3,5-triazines of the formula (II) which have unsubstituted or substituted alkyl radicals in the 6-position. In contrast to aromatic radicals in the 6-position, the alkylthio-1,3,5-triazines which have unsubstituted or substituted aliphatic radicals in the 6-position and which are employed in accordance with the invention generally require milder chlorination conditions. Moreover, the amino group in the 2-position can sometimes lead to undesired side reactions and thus to yield losses or lower product purities

when using the known chlorination conditions.

With a view to the use of the compounds (I) as intermediates for the synthesis of active substances, the radical R^1 preferably has the following meaning:

- R^1 is (C_1-C_6) alkyl which is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, hydroxyl, cyano, nitro, thiocyanato, formyl, (C_1-C_4) alkoxy, (C_1-C_4) alkylthio, (C_1-C_4) alkylsulfinyl, (C_1-C_4) alkylsulfonyl, $[(C_1-C_4)alkyl]carbonyl$, $[(C_1-C_4)alkoxy]carbonyl$, $(C_2-C_4)alkenyl$, $(C_2-C_4)alkynyl$, $(C_3-C_6)cycloalkyl$, phenyl, where each of the last-mentioned 10 radicals is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, (C_1-C_4) alkoxy, $(C_1-C_4)alkylthio$ and, in the case of cyclic radicals, also $(C_1-C_4)alkyl$ and $(C_1-C_4)haloalkyl$.
- R^1 is preferably also $(C_3-C_6)cycloalkyl$ which is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, hydroxyl, cyano, nitro, thiocyanato, formyl, $(C_1-C_4)alkyl$, $(C_1-C_4)alkoxy$, $(C_1-C_4)alkylthio$, $(C_1-C_4)alkylsulfinyl$, $(C_1-C_4)alkylsulfonyl$, $[(C_1-C_4)alkyl]carbonyl$, $[(C_1-C_4)alkoxy]carbonyl$, $(C_2-C_4)alkenyl$, $(C_2-C_4)alkynyl$, $(C_3-C_6)cycloalkyl$, phenyl, where each of the last-mentioned 11 radicals is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, $(C_1-C_4)alkoxy$, $(C_1-C_4)alkylthio$ and, in the case of cyclic radicals, also $(C_1-C_4)alkyl$ and $(C_1-C_4)haloalkyl$.
- R^1 is especially preferably $(C_1-C_6)alkyl$ which is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, preferably fluorine, chlorine or bromine, hydroxyl, methoxy, ethoxy and cyclopropyl.
- R^1 is especially preferably also $(C_3-C_6)cycloalkyl$ which is unsubstituted or substituted by one or more radicals selected from the group

consisting of halogen, preferably fluorine, chlorine or bromine, hydroxyl, (C₁-C₄)alkoxy, preferably methoxy and ethoxy, (C₁-C₄)alkyl, preferably methyl and ethyl, and (C₁-C₄)haloalkyl, preferably CF₃.

R², R³ are preferably in each case independently of one another hydrogen, amino, (C₁-C₆)alkyl, (C₁-C₄)alkylamino, di[(C₁-C₄)alkyl]amino, (C₁-C₄)alkyloxy, (C₃-C₆)cycloalkyl, (C₁-C₄)alkyl]carbonyl, [(C₁-C₄)alkoxy]carbonyl, phenylcarbonyl, phenoxycarbonyl, (C₁-C₄)alkylsulfonyl, phenylsulfonyl or a heterocyclyl radical having 3 to 6 ring atoms and 1 to 3 hetero ring atoms selected from the group consisting of N, O and S, where phenyl in the abovementioned radicals or the heterocyclyl radical independently of one another are unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, preferably fluorine, chlorine or bromine, hydroxyl, (C₁-C₄)alkoxy, preferably methoxy and ethoxy, (C₁-C₄)alkyl, preferably methyl and ethyl, and (C₁-C₄)haloalkyl, preferably CF₃,
or

R², R³ together with the nitrogen atom of the group NR²R³ is a heterocyclic radical which has 3 to 6 ring atoms and 1 to 3 hetero ring atoms, where, in addition to the nitrogen atom, the other hetero ring atoms which may be present are selected from the group consisting of N, O and S and the heterocycle is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, preferably fluorine, chlorine or bromine, hydroxyl, (C₁-C₄)alkoxy, preferably methoxy and ethoxy, (C₁-C₄)alkyl, preferably methyl and ethyl, and (C₁-C₄)haloalkyl, preferably CF₃.

The radicals R², R³ in each case independently of one another are preferably hydrogen, amino, methyl, ethyl, acetyl.

The compounds of the formula (I) can form salts when a basic group such as, for example, amino or alkylamino, undergoes an addition reaction with a

suitable inorganic or organic acid such as, for example, HCl, HBr, H₂SO₄ or HNO₃, but also oxalic acid or sulfonic acids.

With a view to the use of the compounds (II) as intermediates for the synthesis of active substances, the radical X has, for example, the following meaning:

X is, for example, hydrogen, (C₁-C₆)alkyl, (C₂-C₆)alkenyl or (C₂-C₆)alkynyl, where each of the last-mentioned 3 radicals is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, [(C₁-C₄)alkyl]carbonyl, [(C₁-C₄)alkoxy]carbonyl, (C₃-C₆)cycloalkyl and phenyl, each of the last-mentioned 10 radicals being unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio and, in the case of cyclic radicals, also (C₁-C₄)alkyl and (C₁-C₄)haloalkyl or represents phenyl which is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, cyano, nitro, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, [(C₁-C₄)alkyl]carbonyl, [(C₁-C₄)alkoxy]carbonyl, (C₂-C₄)alkenyl, (C₂-C₄)alkynyl, (C₃-C₆)cycloalkyl, each of the last-mentioned 10 radicals being unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio and, in the case of cyclic radicals, also (C₁-C₄)alkyl and (C₁-C₄)haloalkyl, or represents a 2-amino-4-thio-1,3,5-triazine radical which is bonded via sulfur and equally substituted,

X preferably represents (C₁-C₄)alkyl which is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio, (C₃-C₆)cycloalkyl and phenyl, each of the last-mentioned 4 radicals being unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio and, in the case of cyclic radicals, also (C₁-C₄)alkyl and (C₁-C₄)haloalkyl, or

represents phenyl which is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, cyano, nitro, (C₁-C₄)alkyl, (C₁-C₄)haloalkyl, (C₁-C₄)alkoxy, (C₁-C₄)haloalkoxy, (C₁-C₄)alkylthio and [(C₁-C₄)alkoxy]carbonyl, or represents a 2-amino-4-thio-1,3,5-triazine radical which is bonded via sulfur and equally substituted,

X represents, in particular, (C₁-C₄)alkyl, benzyl or phenyl, where each of the last-mentioned two groups is unsubstituted in the phenyl moiety or substituted by one or more radicals selected from the group consisting of halogen, cyano, nitro, (C₁-C₄)alkyl, preferably methyl, (C₁-C₄)haloalkyl, preferably CF₃ or CCl₃, (C₁-C₄)alkoxy, preferably methoxy, (C₁-C₄)haloalkoxy, preferably OCHF₂, and (C₁-C₄)alkylthio.

In the abovementioned formulae, the radicals alkyl, alkoxy, haloalkyl, haloalkoxy, alkylamino and alkylthio and the corresponding unsaturated and/or substituted radicals in the carbon skeleton can in each case be straight-chain or branched. Unless otherwise specified, the lower carbon skeletons, for example those having 1 to 6 carbon atoms, or in the case of unsaturated groups, 2 to 6 carbon atoms, are preferred for these radicals. Alkyl radicals, also in the composite meanings such as alkoxy, haloalkyl and the like, are, for example, methyl, ethyl, n- or i-propyl, n-, i-, t- or 2-butyl, pentyls, hexyls such as n-hexyl, i-hexyl and 1,3-dimethylbutyl, heptyls such as n-heptyl, 1-methylhexyl and 1,4-dimethylpentyl; alkenyl and alkynyl radicals have the meanings of the possible unsaturated radicals which correspond to the alkyl radicals; alkenyl is, for example, allyl, 1-methylprop-2-en-1-yl, 2-methylprop-2-en-1-yl, but-2-en-1-yl, but-3-en-1-yl, 1-methylbut-3-en-1-yl and 1-methylbut-2-en-1-yl; alkynyl is, for example, propargyl, but-2-yn-1-yl, but-3-yn-1-yl, 1-methylbut-3-yn-1-yl.

Cycloalkyl is a carbocyclic saturated ring system having preferably 3-8 carbon atoms, for example cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.

Halogen is, for example, fluorine, chlorine, bromine or iodine. Haloalkyl,

-alkenyl and -alkynyl are alkyl, alkenyl or alkynyl which are partially or fully substituted by halogen, preferably by fluorine, chlorine and/or bromine, in particular by fluorine and/or chlorine, for example monohaloalkyl, perhaloalkyl, CF_3 , CHF_2 , CH_2F , CF_3CF_2 , CH_2FCHCl , CCl_3 , CHCl_2 , $\text{CH}_2\text{CH}_2\text{Cl}$; haloalkoxy is, for example, OCF_3 , OCHF_2 , OCH_2F , $\text{CF}_3\text{CF}_2\text{O}$, OCH_2CF_3 and $\text{OCH}_2\text{CH}_2\text{Cl}$; this also applies analogously to haloalkenyl and other halogen-substituted radicals.

Aryl is a mono-, bi- or polycyclic aromatic system, for example phenyl, naphthyl, tetrahydronaphthyl, indenyl, indanyl, pentalenyl, fluorenyl and the like, preferably phenyl.

A heterocyclic radical or ring (heterocyclyl) can be saturated, unsaturated or heteroaromatic; it preferably contains one or more, in particular 1, 2 or 3, hetero atoms in the heterocyclic ring, preferably selected from the group consisting of N, O and S; it is preferably an aliphatic heterocyclyl radical having 3 to 7 ring atoms or a heteroaromatic radical having 5 or 6 ring atoms. The heterocyclic radical can be, for example, a heteroaromatic radical or ring (heteroaryl) such as, for example, a mono-, bi- or polycyclic aromatic system in which at least 1 ring contains one or more hetero atoms, for example pyridyl, pyrimidinyl, pyridazinyl, pyrazinyl, triazinyl, thienyl, thiazolyl, thiadiazolyl, oxazolyl, isoxazolyl, furyl, pyrrolyl, pyrazolyl and imidazolyl, or is a partially or fully hydrogenated radical such as oxiranyl, pyrrolidyl, piperidyl, piperazinyl, dioxolanyl, oxazoliny, isoxazoliny, oxazolidiny, isoxazolidiny, morpholiny, tetrahydrofuryl. Substituents which are suitable for a substituted heterocyclic radical are the substituents mentioned further below, and additionally also oxo. The oxo group may also occur on the hetero ring atoms, which may exist in various degrees of oxidation, for example in the case of N and S.

Substituted radicals such as a substituted alkyl, alkenyl, alkynyl, aryl, phenyl, benzyl, heterocyclyl and heteroaryl radical, are, for example, a substituted radical derived from the unsubstituted parent structure, the substituents being, for example, one or more, preferably 1, 2 or 3, radicals

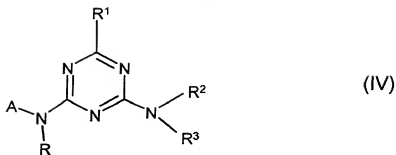
selected from the group consisting of halogen, alkoxy, haloalkoxy, alkylthio, hydroxyl, amino, nitro, carboxyl, cyano, azido, alkoxycarbonyl, alkylcarbonyl, formyl, carbamoyl, mono- and dialkylaminocarbonyl, substituted amino such as acylamino, mono- and dialkylamino, and alkylsulfinyl, haloalkylsulfinyl, alkylsulfonyl, haloalkylsulfonyl and, in the case of cyclic radicals, also alkyl and haloalkyl; the term "substituted radicals" such as substituted alkyl and the like includes, as substituents, in addition to the abovementioned saturated hydrocarbon-containing radicals the corresponding unsaturated aliphatic and aromatic radicals, such as unsubstituted or substituted alkenyl, alkynyl, alkenyloxy, alkynyloxy, phenyl, phenoxy and the like. In the case of radicals having carbon atoms, those having 1 to 4 carbon atoms, in particular 1 or 2 carbon atoms, are preferred. Preferred are, as a rule, substituents selected from the group consisting of halogen, for example fluorine and chlorine, (C₁-C₄)alkyl, preferably methyl or ethyl, (C₁-C₄)haloalkyl, preferably trifluoromethyl, (C₁-C₄)alkoxy, preferably methoxy or ethoxy, (C₁-C₄)haloalkoxy, nitro and cyano. Especially preferred in this context are the substituents methyl, methoxy and chlorine.

The formula (I) and (II) also encompass all stereoisomers. Such compounds contain one or more asymmetric carbon atoms or else double bonds which are not mentioned specifically in the formulae. The stereoisomers which are possible and which are defined by their specific spatial form, such as enantiomers, diastereomers, Z- and E-isomers, can be obtained by customary methods from mixtures of the stereoisomers or else be prepared by stereoselective reactions in combination with the use of stereochemically pure starting materials.

It is preferred to react the compounds (I) with amines of the formula (III)



with exchange of the chlorine atom, to give herbicidal aminotriazines of the formula (IV)



where, in formulae (III) and (IV), the radicals R^1 , R^2 , R^3 are as defined in formula (I) and A and R are radicals which in conjunction with the remaining molecular structure of the formula (IV) constitute the chemical structure of a herbicidally active aminotriazine.

The herbicidal aminotriazines are preferably those from the publications WO-A-90/09378, WO-A-96/25404, WO-A-97/00254, WO-A-97/08156, WO-A-97/19936, WO-A-97/29095, WO-A-97/31904, WO-A-97/35481, WO-A-98/10654, WO-A-98/15536, WO-A-98/15537, WO-A-98/15538, WO-A-98/15539, the International Application No. PCT/EP98/00283 and the German Patent Application No. 19826670.7, which have already been mentioned at the outset, but the radicals R^1 , R^2 and R^3 are as defined in the abovementioned process according to the invention. The definition of the herbicidal aminotriazines from the publications is specifically incorporated by reference; they are thus part of the present description.

In formula (IV), the radical A is preferably a (C_1-C_6) alkylene chain which is substituted in the α -position relative to the amino group by an unsubstituted or substituted alkyl radical and in the ω -position by an unsubstituted or substituted aryl, heteroaryl, aryloxy or heteroaryloxy radical and which can also have further substituents selected from the group consisting of halogen, alkyl, alkoxy and hydroxyl.

R is preferably H or alkyl such as (C_1-C_4) alkyl, in particular H.

Especially preferred are the preferred herbicidal aminotriazines which are

mentioned in the above publications, in particular the compounds which are in each case defined specifically, such as the preparation examples and the individually defined tabulated examples, as long as the radicals which correspond to the radicals R^1 , R^2 and R^3 in formula (IV) are defined within the scope of the present invention.

The invention therefore also relates to a process for the preparation of herbicidal aminotriazines of the formula (IV), which comprises first preparing, in accordance with the invention, a compound of the formula (I) and then reacting it with an amine of the formula (III) to give the compound of the formula (IV).

Reaction conditions for reacting the compounds of the formulae (I) and (III) are known in principle from the publications mentioned in connection with the herbicidal aminotriazines (IV) and from the literature cited therein, or can be carried out analogously to the standard reactions known to the skilled worker for reacting heteroaromatic chlorine compounds with amines.

The invention generally also relates to the use of compounds of the formula (I) or salts thereof which have been obtained by the process according to the invention for the preparation of the compounds (I) for the preparation of bioactive substances from the chemical class of the aminotriazines, preferably the herbicidal aminotriazines.

In the examples which follow, quantities are by weight unless otherwise specified. Conventional abbreviations are used for units and physical quantities, for example

h = hour(s), m.p. = melting point, l = liter, g = gram, min = minute(s),
in vacuo = under reduced pressure

Examples:

a) 2-Amino-4-methylthio-6-(1-fluoroisopropyl)-1,3,5-triazine

125 g of 2-fluoroisobutyryl chloride and 300 ml of triethylamine were simultaneously added dropwise (0.5 h) at approx. 20°C to a solution of 245 g of S-methylguanylisothiurea methylsulfate and 250 g of sodium sulfate in 1 liter of anhydrous N-methylpyrrolidone. After the reaction mixture had been stirred for 3 h at 50°C, the cooled mixture was poured into 5 liters of water. The crude product which has precipitated is filtered off with suction and extracted by stirring with heptane. After filtration with suction and drying, 150 g (75%) of 2-amino-4-methylthio-6-(1-fluoroisopropyl)-1,3,5-triazine were obtained as a white powder (m.p. 155°C).

¹H NMR (CDCl₃): δ = 1.7 (d, 6H), 2.5 (s, 3H), 5.7 (s br., 1H), 6.9 (s br., 1H).

b) 2-Amino-4-chloro-6-(1-fluoroisopropyl)-1,3,5-triazine (Table 1, Example 25)

Chlorine gas was passed at 20 to 25°C into a suspension of 150 g of 2-amino-4-methylthio-6-(1-fluoroisopropyl)-1,3,5-triazine in 1 liter of glacial acetic acid (15 min). The reaction mixture was stirred for 30 min at approx. 20°C, flushed with nitrogen gas for 1 h at room temperature, poured into 5 liters of ice-cold aqueous solution of 350 g of sodium hydroxide and stirred for 5 min. After filtration with suction and drying, 110 g (80%) of 2-amino-4-chloro-6-(1-fluoroisopropyl)-1,3,5-triazine were obtained as a white powder (m.p. 185°C).

¹H NMR (CDCl₃): δ = 1.7 (d, 6H), 6.2 (s br., 1H), 6.9 (s br., 1H).

c) 2-Amino-4-chloro-6-(1-fluoroethyl)-1,3,5-triazine (Table 1, Example 21)

Chlorine gas was passed into a suspension of 38 g of 2-amino-4-methylthio-6-(1-fluoroethyl)-1,3,5-triazine in 0.25 l of glacial acetic acid (15 min) at 20 to 25°C. The reaction mixture was stirred for 30 min at approx. 20°C, sprayed for 1 hour with nitrogen gas at room temperature, poured into 1.25 l of ice-cold aqueous solution of 87 g of sodium hydroxide and stirred for 5 min. After extraction with ethyl acetate, the organic phase was washed with water and dried over magnesium sulfate, and the solvent was removed in vacuo. The crude product was purified by stirring in heptane. After filtration with suction and drying, 25 g (70%) of 2-amino-4-chloro-6-(1-fluoroethyl)-1,3,5-triazine were obtained as a white powder (m.p. 131°C); ^1H NMR (CDCl_3): δ = 1.7 (dd, 3 H), 5.4 (dq, 1 H), 6.1 (s br., 1 H), 6.7 (s br., 1H).

- d) 2-Amino-4-chloro-6-trifluoromethyl-1,3,5-triazine (Table 1, Example 15)

Chlorine gas was passed into a solution of 21 g of 2-amino-4-methylthio-6-trifluoromethyl-1,3,5-triazine in 0.2 l glacial acetic acid at 20 to 25°C (15 min). The reaction mixture was stirred for 30 min at approx. 20°C, sprayed for 1 hour with nitrogen gas at room temperature, poured into 1 l of ice-cold aqueous solution of 70 g of sodium hydroxide and stirred for 5 min. After extraction with ethyl acetate, the organic phase was washed with water and dried over magnesium sulfate, and the solvent was removed in vacuo. The crude product was purified by stirring in heptane. After filtration with suction and drying, 12 g (60%) of 2-amino-4-chloro-6-trifluoromethyl-1,3,5-triazine were obtained as a white powder (m.p. 109°C); ^1H NMR (CDCl_3): δ = 6.4 (s br., 2H).

- e) 2-Amino-4-chloro-6-(1-chloroisopropyl)-1,3,5-triazine (Table 1, Example 32)

Chlorine gas was passed at 20 to 25°C into a suspension of 110 g of

2-amino-4-methylthio-6-(1-chloroisopropyl)-1,3,5-triazine in 0.75 l of glacial acetic acid (30 min). The reaction mixture was stirred for 30 min at approx. 20°C, sprayed with nitrogen gas for 1 h at room temperature, poured into 3.75 l of ice-cold aqueous solution of 260 g of sodium hydroxide and stirred for 5 min. After filtration with suction and drying, 83 g (80%) of 2-amino-4-chloro-6-(1-chloroisopropyl)-1,3,5-triazine were obtained as a white powder (m.p. 110°C); ¹H NMR (CDCl₃): δ = 1.9 (s, 6 H), 6.0 (s br., 2 H)

- f) Comparative example analogous to the chlorination described in US-A-5,084,570 [conditions for (het)aryl-substituted 2-amino-4-alkylthio-1,3,5-triazines]

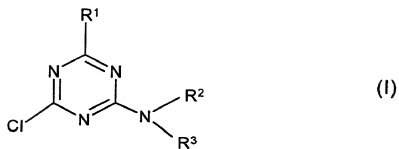
Chlorine gas was passed at 35 to 40°C into a solution of 5 g of 2-amino-4-methylthio-6-(1-chloroisopropyl)-1,3,5-triazine in 0.1 l of trichloromethane (or tetrachloromethane) (15 min). 10 g of potassium carbonate were added to the reaction mixture at room temperature, and the mixture was stirred for 5 minutes and filtered and the solvent removed in vacuo. This gave a product mixture in which approximately 0.5 g (10%) of 2-amino-4-chloro-6-(1-chloroisopropyl)-1,3,5-triazine are present (detection by HPLC comparison with 100% product).

The table which follows shows the abovementioned examples according to the invention in addition to other examples obtained analogously. The chlorination products of the formula (I) are obtained, as a rule, in yields of 60 to 95% of theory.

The following abbreviations are used in Table 1 which follows:




Me	=	methyl
c-Pr	=	cyclopropyl
c-Bu	=	cyclobutyl; n-Bu = n-butyl
c-Pe	=	cyclopentyl
Ac	=	acetyl



Table 1: Compounds of the formula (I)







No.	R ¹	R ²	R ³
1	CH ₃	H	H
2	C ₂ H ₅	H	H
3	C ₃ H ₇	H	H
4	CH(CH ₃) ₂	H	H
5	c-Pr	H	H
6	n-C ₄ H ₉	H	H
7	CH(CH ₃)C ₂ H ₅	H	H
8	c-Bu	H	H
9	n-C ₅ H ₁₁	H	H
10	c-Pe	H	H
11	CH ₂ -c-Pr	H	H
12		H	H
13	CH ₂ F	H	H


No.	R ¹	R ²	R ³
14	CHF ₂	H	H
15	CF ₃	H	H
16	CH ₂ Cl	H	H
17	CHCl ₂	H	H
18	CCl ₃	H	H
19	CClF ₂	H	H
20	CFCl ₂	H	H
21	CHFCH ₃	H	H
22	CF ₂ CH ₃	H	H
23	CF ₂ CF ₂ H	H	H
24	CF ₂ CF ₃	H	H
25	CF(CH ₃) ₂	H	H
26	CH(CF ₃)CH ₃	H	H
27	CF(CF ₃)CH ₃	H	H
28	CH(CF ₃) ₂	H	H
29	CF(CF ₃) ₂	H	H
30	CHClCH ₃	H	H
31	CCl ₂ CH ₃	H	H
32	CCl(CH ₃) ₂	H	H
33	CFCl-CH ₃	H	H



No.	R ¹	R ²	R ³
34		H	H
35		H	H
36	CH ₂ OCH ₃	H	H
37	CH(CH ₃)OCH ₃	H	H
38	C(CH ₃) ₂ OCH ₃	H	H
39	C ₂ H ₅ OCH ₃	H	H
40	CH(CH ₃)CH ₂ OCH ₃	H	H
41		H	H
42	CH ₂ OH	H	H
43	CH(CH ₃)OH	H	H
44	C(CH ₃) ₂ OH	H	H
45	C ₂ H ₅ OH	H	H
46	CH(CH ₃)CH ₂ OH	H	H



No.	R ¹	R ²	R ³
47		H	H
48	CH ₃	Me	H
49	C ₂ H ₅	Me	H
50	C ₃ H ₇	Me	H
51	CH(CH ₃) ₂	Me	H
52	c-Pr	Me	H
53	n-C ₄ H ₉	Me	H
54	CH(CH ₃)C ₂ H ₅	Me	H
55	c-Bu	Me	H
56	n-C ₅ H ₁₁	Me	H
57	c-Pe	Me	H
58	CH ₂ -c-Pr	Me	H
59		Me	H
60	CH ₂ F	Me	H
61	CHF ₂	Me	H
62	CF ₃	Me	H
63	CH ₂ Cl	Me	H


No.	R ¹	R ²	R ³
64	CHCl ₂	Me	H
65	CCl ₃	Me	H
66	CClF ₂	Me	H
67	CFCl ₂	Me	H
68	CHFCH ₃	Me	H
69	CF ₂ CH ₃	Me	H
70	CF ₂ CF ₂ H	Me	H
71	CF ₂ CF ₃	Me	H
72	CF(CH ₃) ₂	Me	H
73	CH(CF ₃)CH ₃	Me	H
74	CF(CF ₃)CH ₃	Me	H
75	CH(CF ₃) ₂	Me	H
76	CF(CF ₃) ₂	Me	H
77	CHClCH ₃	Me	H
78	CCl ₂ CH ₃	Me	H
79	CCl(CH ₃) ₂	Me	H
80	CFCl-CH ₃	Me	H
81		Me	H




No.	R ¹	R ²	R ³
82		Me	H
83	CH ₂ OCH ₃	Me	H
84	CH(CH ₃)OCH ₃	Me	H
85	C(CH ₃) ₂ OCH ₃	Me	H
86	C ₂ H ₅ OCH ₃	Me	H
87	CH(CH ₃)CH ₂ OCH ₃	Me	H
88		Me	H
89	CH ₂ OH	Me	H
90	CH(CH ₃)OH	Me	H
91	C(CH ₃) ₂ OH	Me	H
92	C ₂ H ₅ OH	Me	H
93	CH(CH ₃)CH ₂ OH	Me	H
94		Me	H
95	CH ₃	Me	Me



No.	R ¹	R ²	R ³
96	C ₂ H ₅	Me	Me
97	C ₃ H ₇	Me	Me
98	CH(CH ₃) ₂	Me	Me
99	c-Pr	Me	Me
100	n-C ₄ H ₉	Me	Me
101	CH(CH ₃)C ₂ H ₅	Me	Me
102	c-Bu	Me	Me
103	n-C ₅ H ₁₁	Me	Me
104	c-Pe	Me	Me
105	CH ₂ -c-Pr	Me	Me
106		Me	Me
107	CH ₂ F	Me	Me
108	CHF ₂	Me	Me
109	CF ₃	Me	Me
110	CH ₂ Cl	Me	Me
111	CHCl ₂	Me	Me
112	CCl ₃	Me	Me
113	CClF ₂	Me	Me
114	CFCl ₂	Me	Me
115	CHFCH ₃	Me	Me

No.	R ¹	R ²	R ³
116	CF ₂ CH ₃	Me	Me
117	CF ₂ CF ₂ H	Me	Me
118	CF ₂ CF ₃	Me	Me
119	CF(CH ₃) ₂	Me	Me
120	CH(CF ₃)CH ₃	Me	Me
121	CF(CF ₃)CH ₃	Me	Me
122	CH(CF ₃) ₂	Me	Me
123	CF(CF ₃) ₂	Me	Me
124	CHClCH ₃	Me	Me
125	CCl ₂ CH ₃	Me	Me
126	CCl(CH ₃) ₂	Me	Me
127	CFCl-CH ₃	Me	Me
128		Me	Me
129		Me	Me
130	CH ₂ OCH ₃	Me	Me
131	CH(CH ₃)OCH ₃	Me	Me
132	C(CH ₃) ₂ OCH ₃	Me	Me




No.	R ¹	R ²	R ³
133	C ₂ H ₅ OCH ₃	Me	Me
134	CH(CH ₃)CH ₂ OCH ₃	Me	Me
135		Me	Me
136	CH ₂ OH	Me	Me
137	CH(CH ₃)OH	Me	Me
138	C(CH ₃) ₂ OH	Me	Me
139	C ₂ H ₅ OH	Me	Me
140	CH(CH ₃)CH ₂ OH	Me	Me
141		Me	Me
142	CH ₃	Ac	H
143	C ₂ H ₅	Ac	H
144	C ₃ H ₇	Ac	H
145	CH(CH ₃) ₂	Ac	H
146	c-Pr	Ac	H
147	n-C ₄ H ₉	Ac	H
148	CH(CH ₃)C ₂ H ₅	Ac	H
149	c-Bu	Ac	H

No.	R ¹	R ²	R ³
150	n-C ₅ H ₁₁	Ac	H
151	o-Pe	Ac	H
152	CH ₂ -c-Pr	Ac	H
153		Ac	H
154	CH ₂ F	Ac	H
155	CHF ₂	Ac	H
156	CF ₃	Ac	H
157	CH ₂ Cl	Ac	H
158	CHCl ₂	Ac	H
159	CCl ₃	Ac	H
160	CClF ₂	Ac	H
161	CFCl ₂	Ac	H
162	CHFCH ₃	Ac	H
163	CF ₂ CH ₃	Ac	H
164	CF ₂ CF ₂ H	Ac	H
165	CF ₂ CF ₃	Ac	H
166	CF(CH ₃) ₂	Ac	H
167	CH(CF ₃)CH ₃	Ac	H
168	CF(CF ₃)CH ₃	Ac	H
169	CH(CF ₃) ₂	Ac	H

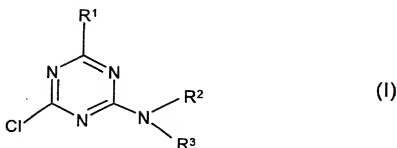
No.	R ¹	R ²	R ³
170	CF(CF ₃) ₂	Ac	H
171	CHClCH ₃	Ac	H
172	CCl ₂ CH ₃	Ac	H
173	CCl(CH ₃) ₂	Ac	H
174	CFCI-CH ₃	Ac	H
175		Ac	H
176		Ac	H
177	CH ₂ OCH ₃	Ac	H
178	CH(CH ₃)OCH ₃	Ac	H
179	C(CH ₃) ₂ OCH ₃	Ac	H
180	C ₂ H ₅ OCH ₃	Ac	H
181	CH(CH ₃)CH ₂ OCH ₃	Ac	H
182		Ac	H
183	CH ₂ OH	Ac	H
184	CH(CH ₃)OH	Ac	H

No.	R ¹	R ²	R ³
185	C(CH ₃) ₂ OH	Ac	H
186	C ₂ H ₅ OH	Ac	H
187	CH(CH ₃)CH ₂ OH	Ac	H
188		Ac	H
189	CH ₃	NH ₂	H
190	C ₂ H ₅	NH ₂	H
191	C ₃ H ₇	NH ₂	H
192	CH(CH ₃) ₂	NH ₂	H
193	c-Pr	NH ₂	H
194	n-C ₄ H ₉	NH ₂	H
195	CH(CH ₃)C ₂ H ₅	NH ₂	H
196	c-Bu	NH ₂	H
197	n-C ₅ H ₁₁	NH ₂	H
198	c-Pe	NH ₂	H
199	CH ₂ -c-Pr	NH ₂	H
200		NH ₂	H
201	CH ₂ F	NH ₂	H

No.	R ¹	R ²	R ³
202	CHF ₂	NH ₂	H
203	CF ₃	NH ₂	H
204	CH ₂ Cl	NH ₂	H
205	CHCl ₂	NH ₂	H
206	CCl ₃	NH ₂	H
207	CClF ₂	NH ₂	H
208	CFCl ₂	NH ₂	H
209	CHFCH ₃	NH ₂	H
210	CF ₂ CH ₃	NH ₂	H
211	CF ₂ CF ₂ H	NH ₂	H
212	CF ₂ CF ₃	NH ₂	H
213	CF(CH ₃) ₂	NH ₂	H
214	CH(CF ₃)CH ₃	NH ₂	H
215	CF(CF ₃)CH ₃	NH ₂	H
216	CH(CF ₃) ₂	NH ₂	H
217	CF(CF ₃) ₂	NH ₂	H
218	CHClCH ₃	NH ₂	H
219	CCl ₂ CH ₃	NH ₂	H
220	CCl(CH ₃) ₂	NH ₂	H
221	CFCl-CH ₃	NH ₂	H

No.	R ¹	R ²	R ³
222		NH ₂	H
223		NH ₂	H
224	CH ₂ OCH ₃	NH ₂	H
225	CH(CH ₃)OCH ₃	NH ₂	H
226	C(CH ₃) ₂ OCH ₃	NH ₂	H
227	C ₂ H ₅ OCH ₃	NH ₂	H
228	CH(CH ₃)CH ₂ OCH ₃	NH ₂	H
229		NH ₂	H
230	CH ₂ OH	NH ₂	H
231	CH(CH ₃)OH	NH ₂	H
232	C(CH ₃) ₂ OH	NH ₂	H
233	C ₂ H ₅ OH	NH ₂	H
234	CH(CH ₃)CH ₂ OH	NH ₂	H
235		NH ₂	H

1. A process for the preparation of compounds of the formula (I) or salts thereof



in which

R¹ is (C₁-C₈)alkyl or (C₃-C₈)cycloalkyl, where each of the two above radicals independently of one another is unsubstituted or substituted,

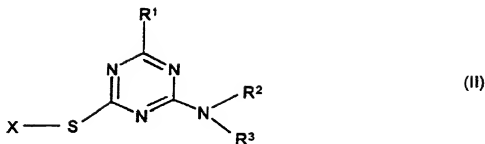
and

R², R³ in each case independently of one another are hydrogen, amino, hydroxyl, formyl or unsubstituted or substituted (C₁-C₈)alkyl, (C₁-C₈)alkylamino, di[(C₁-C₈)alkyl]amino, (C₁-C₈)alkyloxy, aryl, aryloxy, (C₃-C₈)cycloalkyl, [(C₁-C₈)alkyl]carbonyl, [(C₁-C₈)alkoxy]-carbonyl, arylcarbonyl, aryloxy carbonyl, (C₁-C₈)alkylsulfonyl, arylsulfonyl or an unsubstituted or substituted heterocyclyl radical, heterocyclyloxy radical, heterocyclylamino radical, each of which has 3 to 6 ring atoms and 1 to 3 hetero ring atoms selected from the group consisting of N, O and S, or

R², R³ together with the nitrogen atom of the group NR²R³ are a heterocyclic radical having 3 to 6 ring atoms and 1 to 4 hetero ring atoms, where, in addition to the nitrogen atom, the other hetero ring atoms which may exist are selected from the group consisting of N, O and S and the heterocycle is unsubstituted or substituted,

which comprises converting 2-amino-4-thio-1,3,5-triazines of the general

formula (II)



in which X represents hydrogen, (C₁-C₆)alkyl, (C₂-C₆)alkenyl, (C₂-C₆)alkynyl or phenyl, where each of the last-mentioned 4 radicals is unsubstituted or substituted, or represents a 2-amino-4-thio-1,3,5-triazine radical which is bonded via sulfur and equally substituted by chlorination into the compound (I).

2. The process as claimed in claim 1, wherein
 R^1 is (C₁-C₈)alkyl or (C₃-C₈)cycloalkyl, where each of the two abovementioned radicals independently of one another is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, hydroxyl, cyano, nitro, thiocyanato, formyl, (C₁-C₈)alkoxy, (C₁-C₈)alkylthio, (C₁-C₈)alkylsulfanyl, (C₁-C₈)alkylsulfonyl, [(C₁-C₈)alkyl]carbonyl, [(C₁-C₈)alkoxy]carbonyl, (C₂-C₈)alkenyl, (C₂-C₈)alkynyl, (C₃-C₈)cycloalkyl, phenyl and, in the case of cycloalkyl, also (C₁-C₈)alkyl, each of the last-mentioned 11 radicals being unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio and, in the case of cyclic radicals, also (C₁-C₄)alkyl and (C₁-C₄)haloalkyl.

3. The process as claimed in claim 1 or 2, wherein
 R^1 is (C₁-C₆)alkyl which is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, hydroxyl, cyano, nitro, thiocyanato, formyl, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfanyl, (C₁-C₄)alkylsulfonyl, [(C₁-C₄)alkyl]carbonyl, [(C₁-C₄)alkoxy]carbonyl, (C₂-C₄)alkenyl, (C₂-C₄)alkynyl,

(C₃-C₆)cycloalkyl, phenyl, where each of the last-mentioned 10 radicals is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio and, in the case of cyclic radicals, also (C₁-C₄)alkyl and (C₁-C₄)haloalkyl,

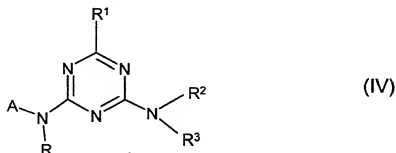
or

(C₃-C₆)cycloalkyl which is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, hydroxyl, cyano, nitro, thiocyanato, formyl, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio, (C₁-C₄)alkylsulfinyl, (C₁-C₄)alkylsulfonyl, [(C₁-C₄)alkyl]carbonyl, [(C₁-C₄)alkoxy]carbonyl, (C₂-C₄)alkenyl, (C₂-C₄)alkynyl, (C₃-C₆)cycloalkyl, phenyl, where each of the last-mentioned 11 radicals is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio and, in the case of cyclic radicals, also (C₁-C₄)alkyl and (C₁-C₄)haloalkyl, and

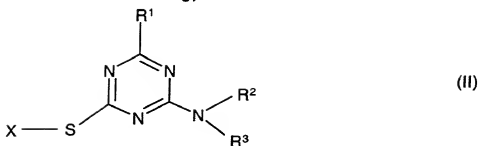
R², R³ in each case independently of one another are hydrogen, amino, (C₁-C₆)alkyl, (C₁-C₄)alkylamino, di[(C₁-C₄)alkyl]amino, (C₁-C₄)alkyloxy, (C₃-C₆)cycloalkyl, (C₁-C₄)alkyl]carbonyl, [(C₁-C₄)alkoxy]carbonyl, phenylcarbonyl, phenoxycarbonyl, (C₁-C₄)alkylsulfonyl, phenylsulfonyl or a heterocyclyl radical having 3 to 6 ring atoms and 1 to 3 hetero ring atoms selected from the group consisting of N, O and S, where phenyl in the abovementioned radicals or the heterocyclyl radical independently of one another are unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, hydroxyl, (C₁-C₄)alkoxy, (C₁-C₄)alkyl, and (C₁-C₄)haloalkyl, or

R², R³ together with the nitrogen atom of the group NR²R³ is a heterocyclic radical which has 3 to 6 ring atoms and 1 to 3 hetero ring atoms, where, in addition to the nitrogen atom, the other hetero ring atoms which may be present are selected from the group consisting of N, O and S and the heterocycle is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, hydroxyl, (C₁-C₄)alkoxy, (C₁-C₄)alkyl and (C₁-C₄)haloalkyl.

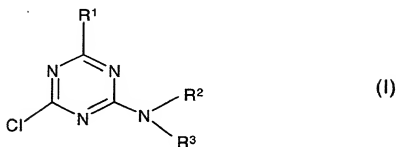
4. The process as claimed in any of claims 1 to 3, wherein a chlorinating agent selected from the group consisting of chlorine, salts of hypochlorous acid, phosphorus pentachloride, phosphoryl chloride and thionyl chloride is employed.
5. The process as claimed in any of claims 1 to 4, wherein the chlorinating agent is employed in an amount of 1 to 100 equivalents based on the compound of the formula (II).
6. The process as claimed in any of claims 1 to 5, which is carried out in the presence of an aprotic or essentially anhydrous protic solvent or mixtures of these.
7. The process as claimed in any of claims 1 to 6, which is carried out at temperatures between -40°C and the boiling point of the solvent in question.
8. The process as claimed in any of claims 1 to 7, which is carried out at temperatures between 0°C and 50°C .
9. A process for the preparation of a herbicidal aminotriazine of the formula (IV) or a salt thereof,



which comprises chlorinating a 2-amino-4-thio-1,3,5-triazine of the formula (II)



to give a compound of the formula (I)



and reacting the resulting compound of the formula (I) with an amine of the formula (III)



to give the herbicidal aminotriazine of the formula (IV), where in formulae (I), (II), (III) and (IV), the radicals R¹, R², R³ and X are as defined in any of claims 1 to 3 and A and R are organic radicals which in conjunction with the residual molecular structure of the formula (IV) constitute the chemical structure of a herbicidally active aminotriazine.

10. The process as claimed in claim 9, wherein A is a (C₁-C₆)alkylene chain which is substituted in the α-position relative to the amino group by an unsubstituted or substituted alkyl radical and in the ω-position by an optionally substituted aryl, heteroaryl, aryloxy or heteroaryloxy radical and which is further unsubstituted or additionally contains further substituents selected from the group consisting of halogen, alkyl, alkoxy and hydroxyl, and

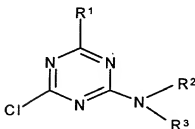
R is hydrogen or alkyl.

11. The use of a compound of the formula (I) or a salt thereof obtained by the process as claimed in any of claims 1 to 8 for the preparation of bioactive substances from the chemical class of the aminotriazines, preferably the herbicidal aminotriazines.

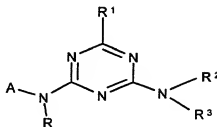
Abstract of the disclosure

Processes for the preparation of 2-amino-4-chloro-1,3,5-triazines

Compounds of the formula (I) or salts thereof

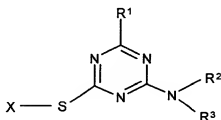


(I)



(IV)

are suitable for preparing active substances from the from the class of the aminotriazines of the formula (IV), for example herbicidal active substances. The compounds (I) can be prepared by chlorinating compounds of the formula (II)



(II)

where, in the formulae, R^1 , R^2 , R^3 and X are as defined in claim 1 and A and R have the meaning required in the active substances to be prepared, and they can be reacted with amines of the formula A-NH-R to give the active substances

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Processes for the preparation of 2-amino-4-chloro-1,3,5-triazines

the specification of which

- is attached hereto

- was filed on July 2, 1999 as International Application PCT/EP99/04581

and including all the amendments through the date hereof.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s) for which Priority is Claimed:

Federal Republic of Germany, 198 30 902.3 of July 10, 1998

And I hereby appoint

William F. Lawrence, Registration No. 28,029, of the firm FROMMER LAWRENCE & HAUG, LLP whose post office address is 745 Fifth Avenue, New York, New York 10151, or their duly appointed associate, my attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to file continuation and divisional applications thereof, to receive the Patent, and to transact all business in the Patent and Trademark Office and in the Courts in connection therewith, and specify that all communications about the application are to be directed to the following correspondence address:

William F. Lawrence, Esq.
c/o FROMMER, LAWRENCE & HAUG LLP
745 Fifth Avenue
New York, New York 10151

Direct all telephone calls
to: (212) 588-0800, to the
attention of:
William F. Lawrence

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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